

Mercury content in ash of solid fuels

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Mercury emission field measurements were conducted for two types of coal from Polish mines. Total mercury content were evaluated in coal and ash on mercury analyzer atomic absorption spectrometer AMA 254. Obtained result shows that brown coal contains more mercury compared to hard coal (289 ppb and 66 ppb respectively for a polydisperse system). Mercury concentration in ashes is several times higher than for coal which means ash may be a good absorber for mercury. Also, application of oxy-fuel technology results in smaller amount of mercury absorbed in the ash which can be related to higher emission of Hg in the gaseous form.

Key words: mercury in coal, mercury in ash, oxy-fuel combustion

Introduction

Background

Global anthropogenic mercury emission is determined at a level of 1930 tonnes per year and comes mainly from the cement, iron and steel industry (mainly non-ferrous metals - Al, Cu, Pb, Zn), mining (gold), power energy industry, and as a consequence of waste disposal. Combustion of solid fuels, known as conversion of chemical energy into electricity, is almost 50% of a global anthropogenic origin of mercury in the environment (Fig.1.). It is estimated that the power plant stacks emit annually into the atmosphere about 880 tonnes of mercury [1]. As shown in Figure 2, large majority of mercury emission, more than 1,200 tonnes per year, belongs to Asian countries. On almost every continent about 50-percent share of global emissions is caused by combustion of fossil fuels. An exception is South America, where 80% of the mercury comes from the gold mining industry, where it is used for purpose of amalgamation (method of extracting noble metals from ore using mercury). Atmosphere pollution with mercury compounds has transgenic character and applies to the entire globe without excluding locations with zero emissions of Hg. Due to the long distance of transport of elemental mercury by the atmosphere and extremely long breakdown time, the control of mercury emission requires cooperation of countries from around the world to achieve a significant improvement.

Physical and chemical properties of mercury. The impact on the environment and living organisms

Mercury is a chemical element from the group of transition metals located in the the 12th group of the periodic table

between gold and thallium. It is the only metal which is in a liquid form at ambient conditions. Mercury occurs mainly in the form of three minerals: cinnabar HgS, calomel Hg₂Cl₂ and especially in a form of elemental mercury [2]. Basic general information and physical properties are shown in Table 1.

Major concentration of the element mercury in solid form on the Earth is present in coal, bituminous shale and bituminous alkaline rocks. Mercury in the form of gas has a high durability and bioaccumulative properties. In the water, soil and living organisms elemental mercury is transformed into complex compounds such as methylmercury

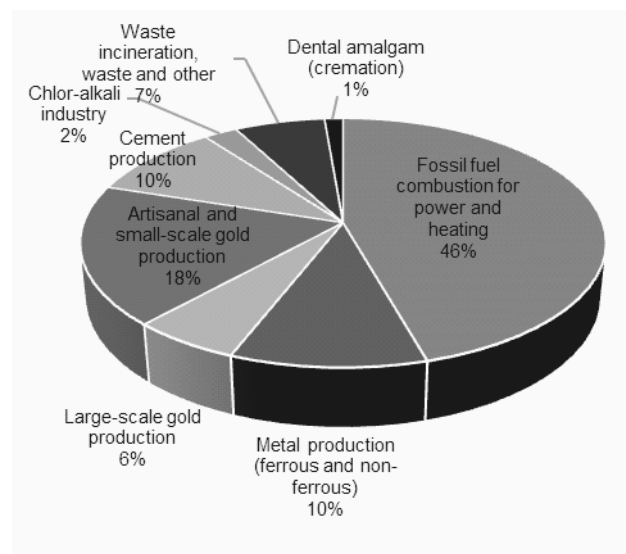


Fig. 1. Relative contributions to estimated emissions to air from anthropogenic sources in 2005 [1]

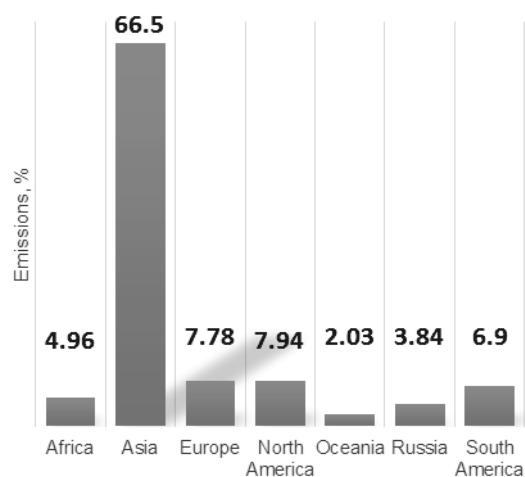


Fig. 2. Mercury emissions to atmosphere from 2005 divided into continents [1]

- the most toxic form of mercury. [3] Scientific research shows an adverse effects of Hg on the root of the nervous system, heart and liver. Mercury causes neurological adverse effects especially in children. [4]

Mercury presence in coals

The quantity of mercury in coals varies and ranges from 50 to 400 ppb (particle per billion). Hard coals contain the lowest values of the Hg (50 - 150 ppb), while brown coals contain the largest values (120 - 400 ppb) [5]. Mercury in coal is released during combustion. Power plants emit most of mercury in the elemental form (Hg^0). Nevertheless, Hg can be oxidized below 540°C by compounds such as SO_2 , H_2O , or HgCl_2 to HCl (g), HgO (g), HgSO_4 (g) and HgS (g). In this form mercury can be absorbed by the ash, which consists of mercury compounds in a solid form: HgCl_2 (s), HgO (s), HgSO_4 (s) and HgS (s). It is estimated that for each 500 MW conventional power plant, 1% of Hg remains in the bottom ash, 60% is attached to the fly ash, 4.7% is removed in the SO_x scrubber and about 30% is emitted into the atmosphere. Hg emission depends mainly on the choice of combustion technology and the conditions under which combustion is achieved [6]. Mercury emission from the Polish power plants is estimated at 13-14 tonnes per year with a consumption of 130 million tonnes of coal, where in the United States 1 billion of carbon generates 49 tons of mercury per year. [2]

Research methodology

Experimental

Two types of coal from Polish mines were chosen for investigation: brown and hard coal. Analytical and hygroscopic moisture was removed in a dryer. Obtained material was grinded in a laboratory cross-beater mill Retsch SK 100 comfort.

Ashing process was carried out in a flow reactor (DTF drop tube furnace showed on Fig.3.) giving a laboratory scale conditions close to real ones (boilers equipped with pulverized fuel burning system).

The atmosphere modification system includes FTIR gas analyzer which controls the oxidant composition and mass flow Vögtlin Instruments AG PCU-10 + GSC-D9SA-BB12, which generate flows of the order of 60l/min.

The atmosphere in the furnace was monitored by the on-line FTIR analyzer, which allowed to keep the parameters constant while generating excess air on level about $\lambda = 1.15-1.3$. The atmosphere modification parameters for oxy-fuel combustion flows was calculated, so that flow rate

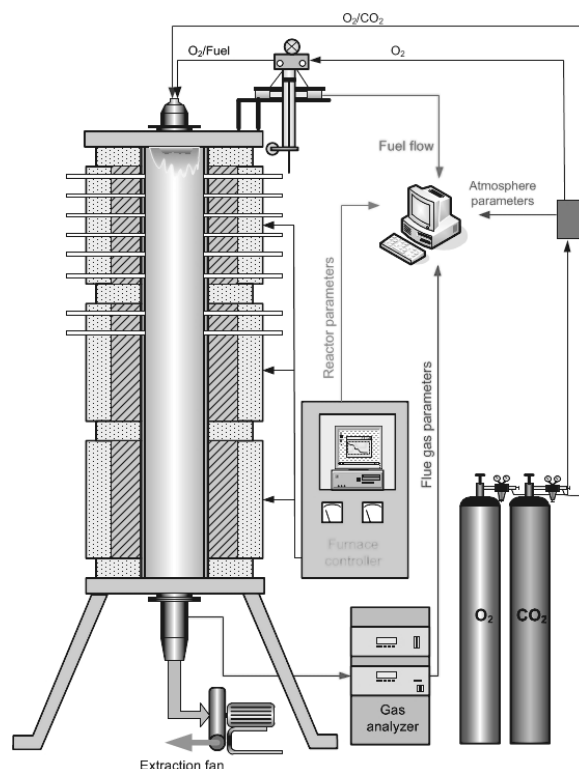


Fig. 3. 3-meter long Drop Tube Furnace

Tab. 1. Preparation of the experimental material

Experimental material	Preparation
Coal	- coal exsiccation, - coal grinding to grain $<500 \mu\text{m}$, - coal fractionation 0-40; 40-100; 100-200 and $>200 \mu\text{m}$
Ash	- coal exsiccation, - coal grinding to grain $<500 \mu\text{m}$, - ashing of coal in the drop tube furnace based on modified atmosphere, - fractionation of ash 0-40, 40-100, 100-200 and >200 microns

of oxygen was identical to the combustion in air conditions and the heat load of the chamber was constant in time. The aim of fractionation is to clearly identify the possibility of accumulation of mercury compounds by ashes. To obtain required fraction, laboratory vibrating screen Retsch AS 400 Control was used. Preparation procedures of coal and ash are shown in Table 1.

Analysis of mercury content in ash

Mercury compounds contents were evaluated in coal and ash on mercury analyzer AMA 254. This is an atomic absorption spectrometer (AAS) designed to detect the total mercury content in solid and liquid samples according to standard ASTM Method D-6722: “Total Mercury in Coal and Combustion Residues”. Analysis processes consist of three main parts:

1. decomposition phase – stage where a sample is placed inside the furnace tube and heated in c.a. 750°C to receive required decomposition of mercury into a gaseous form. After that, in the second part of the tube, evolved gas cleaned from impurities like ash, minerals and moisture are transported.
2. collection phase – stage where evolved clean gas is transported to an amalgamator. There, on glass tube containing gold-plated ceramics all of the mercury is collected.

3. detection phase- After heating amalgamator to 900 °C, mercury is transported in gaseous form to the last stage called detection phase. During this process all mercury pass through the cuvette. The cuvette is positioned in the path length of a standard atomic absorption spectrometer (AAS) which uses lamp with light at a wavelength of 253,7 μm. This wavelength of light is absorbed by mercury particles and detected by a silicon UV detector. [7].

Results and discussion

The first experiment was performed with use of different types of coal. Mercury contents were compared for polydisperse systems and the fractional distribution. The results are shown in Table 2

Fractional distribution shows that in brown coal almost half of all fractions is the fraction <45 microns. Fraction 45-100 has a share of 32% and the fraction of 100-200 is 20% of the entire grains. Noteworthy is negligible fraction above 200, which represents only 2% of the coal. For hard coal the largest share accounts for fraction of 45-100 microns. In comparison, <45 microns fraction is significantly lower in hard coal (21%) and fraction >200 microns is about ten-fold higher (19%). 100-200 fraction accounts for 25% of all particles.

Tab. 2. Mercury content in coal

Fraction	Hard coal		Brown coal	
	Mercury content , ppb	Fractional distribution, %	Mercury content , ppb	Fractional distribution, %
Polydisperse	66,02	100%	288,60	100%
< 45	92,64	21%	308,25	46%
45 - 100	62,99	36%	338,75	32%
100 - 200	75,27	25%	258,88	20%
200 <	82,71	19%	227,61	2%

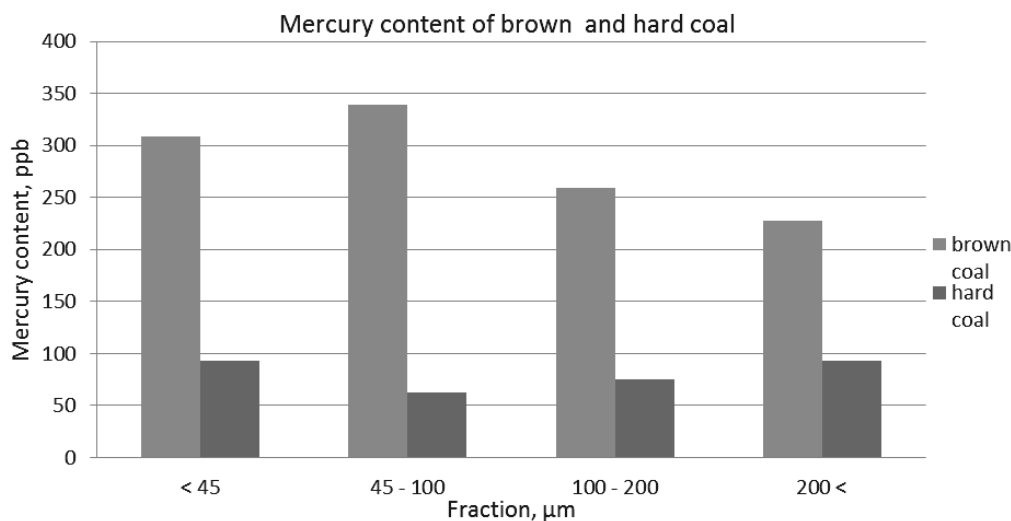


Fig. 4. Mercury content of brown and hard coal

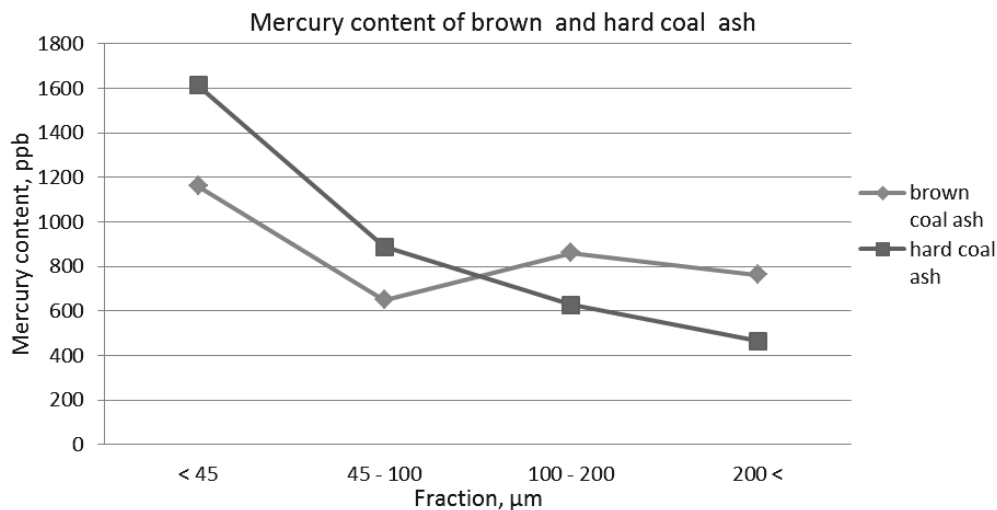


Fig. 5. Mercury content of brown and hard coal ash

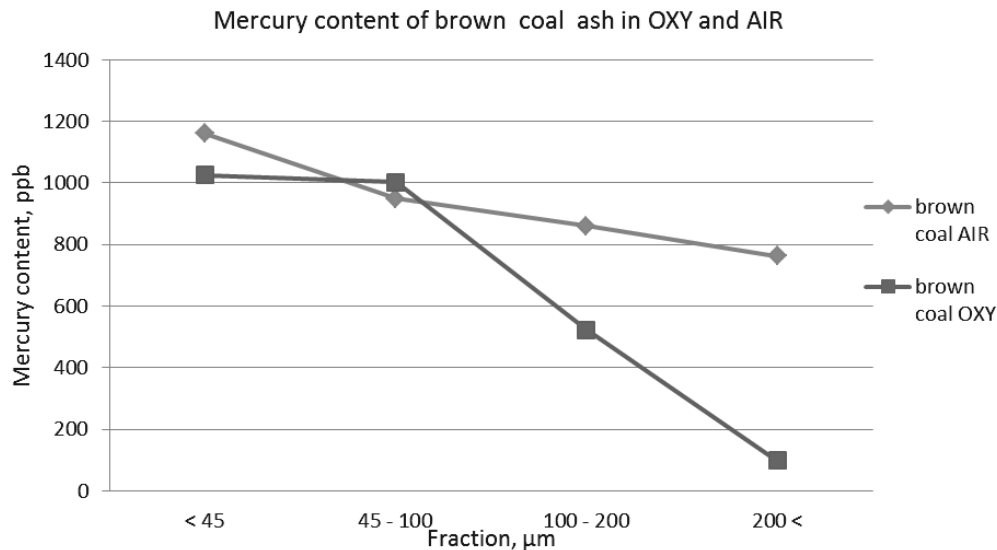


Fig. 6. Mercury content of brown coal ash in OXY and AIR

Analysis of mercury shows that the concentration of Hg in brown coal is four times higher (for a polydisperse system) and from 2.5 to 5.4 times higher for specific fractions. For brown coal maximum Hg concentration occurs for fraction 0 – 45 and 45 - 100 microns. 82% of the total mercury content in brown coal is accumulated in the fraction of 0 - 100 microns. For hard coal differences in concentration range from 66.02 to 92.64 ppb. Simultaneously, the total content of mercury is proportionally distributed between fractions and distribution is approximately 25% (by mass) in each of fractions.

The second part of our studies was to evaluate mercury content in ash from brown and hard coal. The experiment showed that the mercury content in the ash is several times higher than in raw coal. It indicates a high absorption ca-

capacity of ash, which is consistent with current knowledge [8]. The sintering temperature and consequently the porosity of samples can be an important factor in the process of mercury retention in the ash. A well-developed porous structure may be a potential absorber reducing Hg emissions to the atmosphere and at the same time bonding it in solid form.

The impact of atmosphere on the final concentration of mercury in the ash was investigated. The first examined atmosphere was air. It consisted of approximately 21% of oxygen and 79% of nitrogen. The second atmosphere was the one used for the oxy-fuel combustion process. It contained 30% oxygen and 70% carbon dioxide. Parameters of the combustion process in the DTF were selected in a such way, that the oxygen flow rate in each case was similar.

For almost each fraction sample of brown coal lower levels of mercury in OXY technology were observed. Balance of mercury: raw coal/OXY ash/ash AIR indicated a much greater potential for absorption of ash from traditional combustion and consequently increased emissions of mercury in gaseous form.

Conclusions

1. Brown coal contains more mercury compared to hard coal,
2. The largest accumulation of mercury occurs in the smallest fractions,
3. Mercury concentration in ashes is several times higher than for coal,
4. Fly ash (fine fraction of ash) may be a good absorber for mercury,
5. Application of oxy-fuel technology results in smaller amount of mercury absorbed in the ash which can be related to higher emission of Hg in the gaseous form.

Acknowledgements

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